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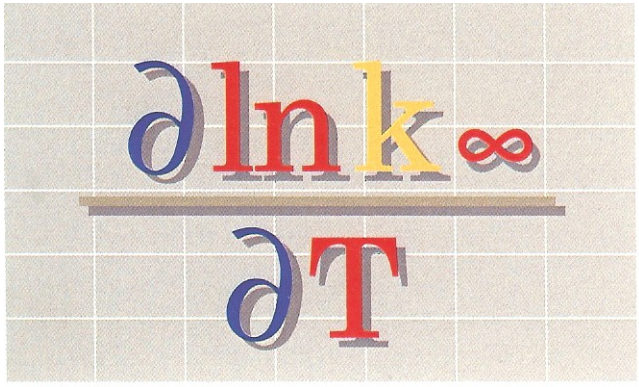
Library of Chemical Kinetic Models for Scientist®



Scientist Chemical Kinetic Library rev. A14E.

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Introduction

The models in this library are intended to aid those users of Scientist who are working on chemical kinetic problems. It is not intended to be a comprehensive resource for information on chemical kinetic models. It is assumed throughout this manual that the user is familiar with the types of problems that are used here and of the appropriate units for each of the variables or parameters. It is also assumed that the user is familiar with the use of Scientist. Please refer to the Scientist User Handbook if you have questions regarding how to run Scientist.

The models in this library are documented in roughly the same manner as the example problems at the end of the Scientist User Manual. The equations defining the model are given followed by the form they will take in Scientist. A sample data set and initial parameter values are given for each model and the results of the least squares fitting for the models are shown. The method used in obtaining the results for these models should not be taken as the ideal method of finding the solution to any particular problem. The examples are given only to demonstrate what may be done with each model and how the output might appear.

A Note on Fitting with Multiple Parameters

The examples worked out in this manual generally involve fitting more than one parameter to the data set used in each problem. Often, there are parameters that could be used to fit the data which are held constant, such as the initial concentrations of the reactants or products. These parameters can be selected for fitting, but some care should be taken in doing so primarily because increasing the number of parameters to be fitted causes the ability to accurately determine the parameters to decrease. In these cases, it is often necessary to fit some of the parameters while holding the others constant, then fit the others while holding the parameters that were originally fit constant, and then fitting all of them together. This method tends to decrease the difficulty of converging to the final solution, but it may not increase the accuracy of the parameter values. We leave it to the users of this library to determine what method is appropriate for the problems being solved.

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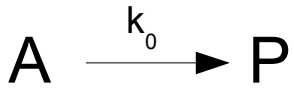
Model #1: Zero-Order Irreversible Reaction



This model may be used in several different ways. First, it can be used to find the reaction rate, K0, given the initial concentration of A, A0, the initial concentration of P, P0, and a number of measurements of the reactant, A, and the product, P, over a period of time. Second, it can be used to model the concentration of the reactant, A, given the initial concentration of P, the initial concentration of A, and a number of measurements of P over a period of time. Third, it can be used to model the concentration of the product, P, given the initial concentration of A, the initial concentration of P, and a number of measurements of A over a given time interval. For the example below, we have chosen the first of these options, that is, to find the reaction rate constant, K0.

The model is as follows:

// Model #1 - Zero-Order Irreversible Reaction

IndVars: T

DepVars: A, P

Params: AO, PO, KO

A = AO-KO*T
P = PO+KO*T

For this example, we need a number of measurements of the concentration of A and the concentration of P. We generate an example data set by choosing some initial values for the parameters A0, P0, and K0. We then do a simulation with these parameter values and randomly add or subtract 0.01 to provide some uncertainty in the data. This data set is as follows:

T	A	P
0	1	0.2
3	0.93	0.26
6	0.88	0.33
9	0.82	0.38
12	0.77	0.43
15	0.7	0.5
18	0.63	0.55
21	0.59	0.63
24	0.52	0.68
27	0.46	0.74
30	0.41	0.8

The parameter values which were used to obtain this data set are shown below. These values will also serve as our initial estimates for a least squares fitting for K0. We will not perform a simplex search because these values should be close enough to the final solution. A more rigorous approach to this problem would include a simplex search

to show that no better solutions exist close to the one found by the least squares fit. We will only attempt to find one solution to this problem.

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
AO	1	0	INF	Y	N
PO	0.2	0	INF	Y	N
KO	0.02	0	INF	N	N

We now proceed with a least squares fit holding A0 and P0 fixed. We find that the best fit value of K0 is:

$$K0 = 0.019935$$

Which is very close to our initial value of 0.02. The sum of squared deviations at this point is 0.00087078 which is good considering the perturbations in the data. If we had not modified our data set by such a large factor we could have obtained a better fit, but it is noteworthy that the model produces reasonable results even if the data is somewhat inaccurate.

To get further information on how well the calculated curve fits our data set we need to look at the statistical output. This output is as follows:

Data Set Name: Model #1

	Weighted	Unweighted
Sum of squared observations:	8.9349	8.9349
Sum of squared deviations:	0.00087078	0.00087078
Standard deviation of data:	0.0064394	0.0064394
R-squared:	0.9999	0.9999
Coefficient of determination:	0.99913	0.99913
Correlation:	0.99958	0.99958
Model Selection Criterion:	6.9581	6.9581

Confidence Intervals

Parameter Name:	KO	
Estimated Value:	0.019935	
Standard Deviation:	7.7353E-005	
95% Range (Univariate):	0.019774	0.020096
95% Range (Support Plane):	0.019774	0.020096

Variance-Covariance Matrix

5.9835E-009

Correlation Matrix

1

Residual Analysis

The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-1.1155	Is probably not significant
Skewness	-0.50302	Is probably not significant
Kurtosis:	-0.38038	Is probably not significant
Weighting Factor:	0	
Heteroscedacticity:	-0.060377	
Optimal Weighting Factor:	-0.060377	

We find that several things are worth looking at in these statistics. First, the confidence limits for K0 are identical to the range initially calculated which implies that there are no solutions close to the one that we found. Also, the standard deviation of these limits is quite small which is very desirable. And lastly, the goodness-of-fit statistics indicate that we obtained a reasonably good fit which is perhaps as good as we can expect for this data set. A plot of the simulated curve and the data set is shown in the following Figure 1.1.

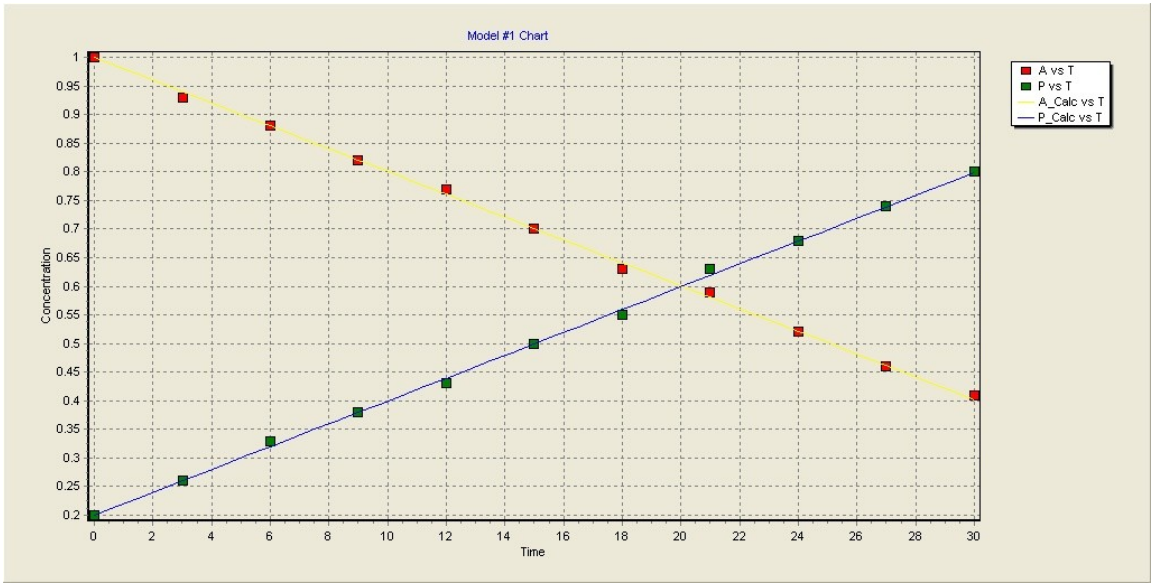
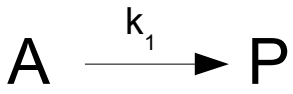


Figure 1.1 – Model #1 Zero Order Irreversible Reaction

We conclude from the above calculations that we have found a good value for the reaction rate with confidence limits that are quite close to it. We also see that the calculated curve fits the data set quite well. Given the simplicity of the model, and simulated accuracy of the data, this result is about what we would expect.

Model #2: First-Order Irreversible Reaction



There are several possible uses for this model. First, and most importantly, it can be used to find the reaction rate, K1, given the initial concentration of A, A0, the initial concentration of P, P0, and a number of measurements of the concentration of the reagent, A, and the product, P, over some time interval. Second, it can be employed to simulate the concentration of P given the initial concentration of P, P0, the initial concentration of A, A0, and a number of measurements of A over a period of time. Third, it can be used to simulate the concentration of A given the initial concentration of P, P0, the initial concentration of A, A0, and a number of measurements of P over a period of time. For Model #1, we produced output similar to the first case, so for this model, we will simulate the concentration of the product, P. The form of the model used to do this is:

// Model #2 - First-Order Irreversible Reaction

IndVars: T

DepVars: A, P

Params: AO, PO, K1

A = AO*EXP((-K1)*T)
P = PO+AO*(1-EXP((-K1)*T))

The data set used to find the concentration of P over a time interval was generated by selecting some initial parameter values, doing a simulation for A, and introducing small errors into the data. We proceed in this manner in order to produce data which approximates experimental measurements. The data set is as follows:

T	A
0	0.5
3	0.43
6	0.38
9	0.31
12	0.27
15	0.24
18	0.2
21	0.18
24	0.15
27	0.13
30	0.11

The parameter values that were used to generate this data will also be used as the starting values of the least squares fitting. These values are used instead of the values obtained from a simplex search for demonstration. Any other application of this model should be preceded by a simplex search unless other conditions apply. These initial parameter values are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
AO	0.5	0	INF	Y	N
PO	0.1	0	INF	Y	N
K1	0.05	0	INF	N	N

We now make sure that P is deselected and A is selected for fitting. We fix A0 and P0 since they are known and do a fitting only for K1. The values of K1 that best fits the data for A is:

K1 = 0.050049

The sum of squared deviations for this fit is 0.00024258 which is not too bad considering the size of the errors in the data for A. We now take a look at the statistics for this fit to assure ourselves that the fit is good enough for simulating P. These statistics are shown below.

Data Set Name: Model #2

	Weighted	Unweighted
Sum of squared observations:	0.9298	0.9298
Sum of squared deviations:	0.00024258	0.00024258
Standard deviation of data:	0.0049253	0.0049253
R-squared:	0.99974	0.99974
Coefficient of determination:	0.99853	0.99853
Correlation:	0.99927	0.99927
Model Selection Criterion:	6.3421	6.3421

Confidence Intervals

Parameter Name:	K1	
Estimated Value:	0.050049	
Standard Deviation:	0.00048924	
95% Range (Univariate):	0.048959	0.051139
95% Range (Support Plane):	0.048959	0.051139

Variance-Covariance

2.3935E-007

Correlation Matrix

1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-1.2885	Is probably not significant
Skewness	0.81981	Is probably not significant
Kurtosis:	0.48551	Is probably not significant
Weighting Factor:	0	
Heteroscedacticity:	0.87949	
Optimal Weighting Factor:	0.87949	

We can see that these figures are not quite as good as we would like them to be. In particular, the goodness-of-fit statistics are rather average and the confidence limits are probably a bit wider than we would like. However, for this particular demonstration, they are probably good enough.

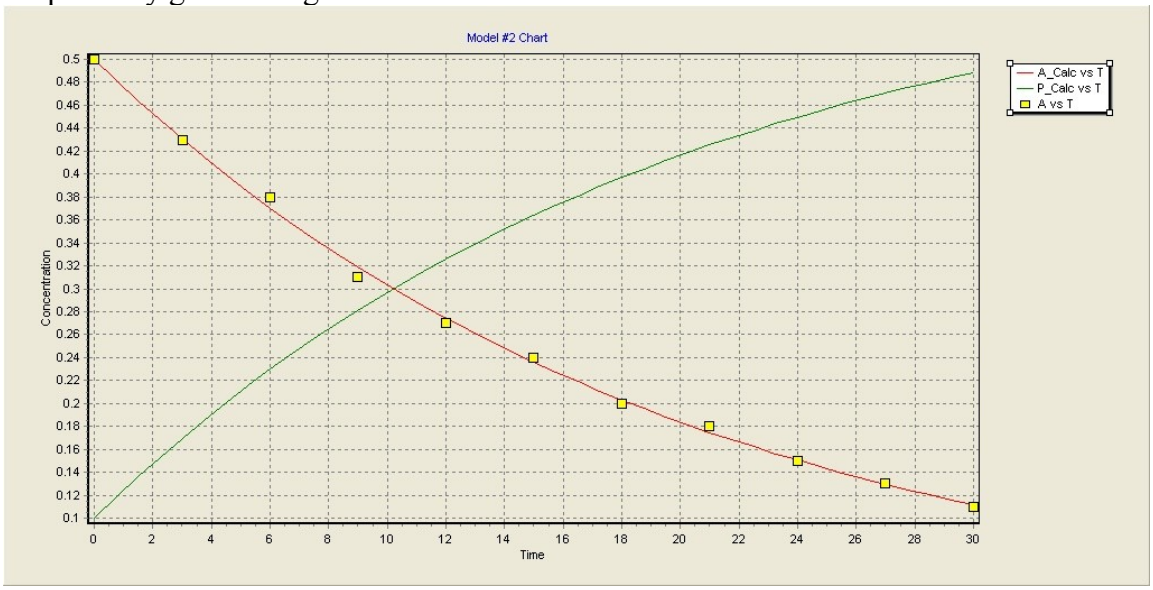
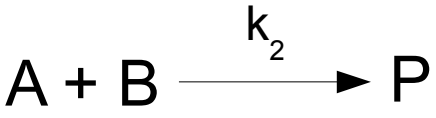


Figure 2.1 – Model #2 First-Order Irreversible Reaction

Model #3: Second-Order Irreversible Reaction



$$A_0 = B_0$$

This model has several possible uses. First, it may be employed to find the second-order reaction rate, K2, given the initial concentration of the reagent A, A0, the initial concentration of the product P, P0, and a number of measurements of the concentration of A and P over time. Second, it can be used to simulate the concentration of P given the initial concentration of P, P0, the initial concentration of A, A0, and a number of observations of A over a period of time. Third, it can simulate the concentration of A given the initial concentration of P, the initial concentration of A, and a number of measurements of the concentration of P over a time interval. We choose to employ the first option, finding the reaction rate, for this example. The model used for this purpose is as follows:

// Model #3 - Second-Order Irreversible Reaction

IndVars: T

DepVars: A, P

Params: AO, PO, K2

A = AO/(1+K2*AO*T)
P = PO+K2*SQR(AO)*T/(1+K2*AO*T)

A data set containing observations of A and P over a period of time was generated by performing a simulation with an initial set of parameter values. The numbers obtained by this method were then rounded to two decimal places after the decimal in order to obtain reasonable errors. These sorts of errors could have been produced by experimental measurements but for this demonstration they are more easily generated by simulation. The data set used for this model is:

T	A	P
0	2.5	0
3	0.77	1.73
6	0.45	2.05
9	0.32	2.18
12	0.25	2.25
15	0.20	2.3
18	0.17	2.33
21	0.15	2.35
24	0.13	2.37
27	0.12	2.38
30	0.11	2.39

The parameter values used to generate this data set are shown below. These values will also be the initial values for the least squares curve fitting. For this example the usual simplex search will not be done since we are not attempting to show that our answer is the best that we can find. Instead we just want to demonstrate the general method for working with the model and produce some sample output to show what sort of curves this model can generate.

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed	Linear Factorization
AO	2.5	0	INF	Y	N
AO	2.5	0	INF	Y	N
PO	0	-1	INF	Y	N
K2	0.3	0	INF	N	N

We perform a least squares curve fit for the reaction rate K2 by selecting only this parameter and deselecting A0 and P0. The result of this fitting is as follows:

K2 = 0.30117

The sum of squared deviations for this value of K2 is 0.00012370 which is reasonably good considering that the data was slightly perturbed. We now check to see how good the fit was according to other statistics. The summary of these statistics is the following:

Data Set Name: Model #3

	Weighted	Unweighted
Sum of squared observations:	57.59	57.59
Sum of squared deviations:	0.0001237	0.0001237
Standard deviation of data:	0.002427	0.002427
R-squared:	1	1
Coefficient of determination:	0.99999	0.99999
Correlation:	1	1
Model Selection Criterion:	12.052	12.052

Confidence Intervals

Parameter Name:	K2	
Estimated Value:	0.30117	
Standard Deviation:	0.00063318	
95% Range (Univariate):	0.29986	0.30249
95% Range (Support Plane):	0.29986	0.30249

Variance-Covariance Matrix

4.0091E-007

Correlation Matrix

1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	0.14459	Is probably not significant
Skewness	4.5459E-014	Is probably not significant
Kurtosis:	-1.3242	indicates the presence of a few large residuals of either sign.
Weighting Factor:	0	
Heteroscedacticity:	-1.381E-014	
Optimal Weighting Factor:	-1.3767E-014	

It is instructive to note that the goodness-of-fit statistics and the confidence limits on the parameters are both quite good. We might expect that the data errors would not allow such a good fit, but the model is not too complicated to provide us with good limits on the parameters.

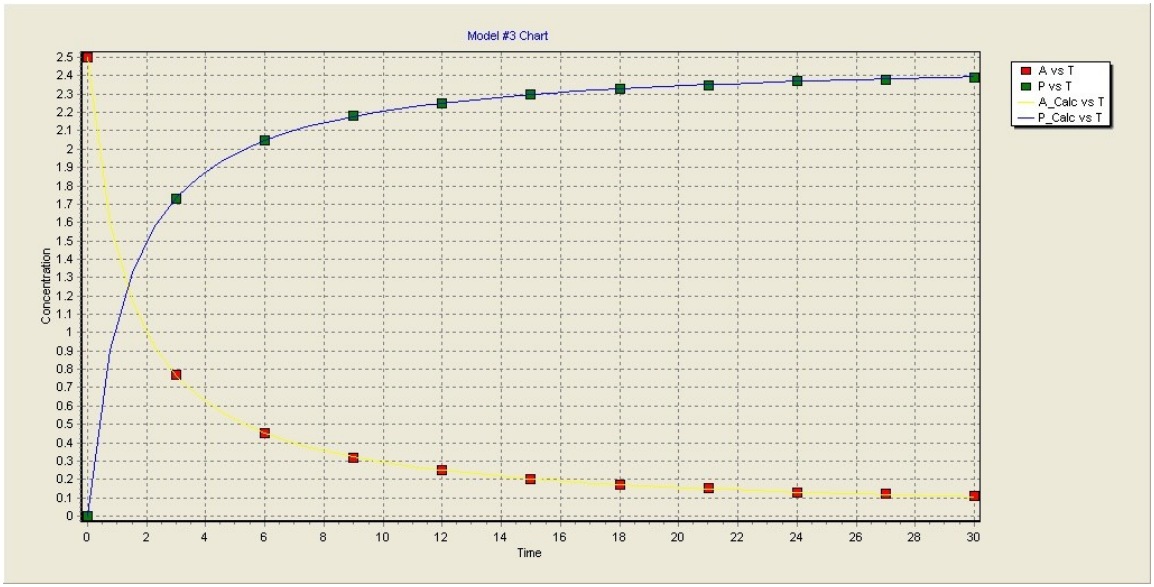
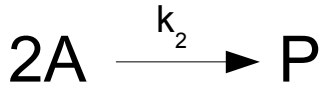


Figure 3.1 – Model #3 Second-Order Irreversible Reaction

Model #4: Second-Order Irreversible Reaction



This model is useful for several different calculations. It may be used to compute the reaction rate, K2, given the initial concentration of A, A0, the initial concentration of P, P0, and a number of measurements of the concentrations of the reagent, A, and the product, P, over a period of time. It can also be used to simulate either the concentration of A or the concentration of P given a number of measurements of the concentration of the other variable over time and the initial concentrations of both variables. In this example, we will compute the reaction rate. The model used for these calculations is:

// Model #4 - Second-Order Irreversible Reaction

IndVars: T

DepVars: A, P

Params: AO, PO, K2

A = AO/(1+2*K2*AO*T)
P = PO+2*K2*AO^2*T/(1+2*K2*AO*T)

The measurements of the concentrations of A and P were generated for this example by performing a simulation with initial parameter values. For any other application, the concentrations would have been measured experimentally. The data set is as follows:

T	A	P
0	1.3	0.2
4	0.99	0.51
8	0.8	0.7
12	0.67	0.83
16	0.58	0.92
20	0.51	0.99
24	0.45	1.05
28	0.41	1.09
32	0.37	1.13
36	0.34	1.16
40	0.32	1.18

The initial parameter values used to generate the data set are also the values that will be used to begin the least squares curve fitting. We do this only for demonstration. A simplex search is recommended for other applications of this model. The initial parameter values are as follows:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
AO	1.3	0	INF	Y	N
PO	0.2	0	INF	Y	N
K2	0.03	0	INF	N	N

The least squares curve fitting is performed by selecting only K2 for fitting and then starting the calculation. The value that Scientist finds as the best-fit solution is:

K2 = 0.029988

The current sum of squared deviations for this fit is 9.1983E-5 which indicates that the simulated points match the data points very well. To see just how well they match, we need to look at the summary of statistics which is shown below.

Data Set Name: Model #4

	Weighted	Unweighted
Sum of squared observations:	14.692	14.692
Sum of squared deviations:	9.1983E-005	9.1983E-005
Standard deviation of data:	0.0020929	0.0020929
R-squared:	0.99999	0.99999
Coefficient of determination:	0.99996	0.99996
Correlation:	0.99998	0.99998
Model Selection Criterion:	10.043	10.043

Confidence Intervals

Parameter Name:	K2	
Estimated Value:	0.029988	
Standard Deviation:	4.9312E-005	
95% Range (Univariate):	0.029886	0.030091
95% Range (Support Plane):	0.029886	0.030091

Variance-Covariance Matrix

2.4317E-009

Correlation Matrix

1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-1.4506	Is probably not significant
Skewness	3.8415E-013	Is probably not significant
Kurtosis:	-0.32348	Is probably not significant
Weighting Factor:	0	
Heteroscedacticity:	8.626E-015	
Optimal Weighting Factor:	8.6597E-015	

These numbers indicate that the fit of the simulated curve to the data was quite good. The confidence limits for the K2 are very well determined and the Model Selection Criterion is relatively high indicating a good fit. We conclude from this that the model is capable of producing quite good results from experimental data.

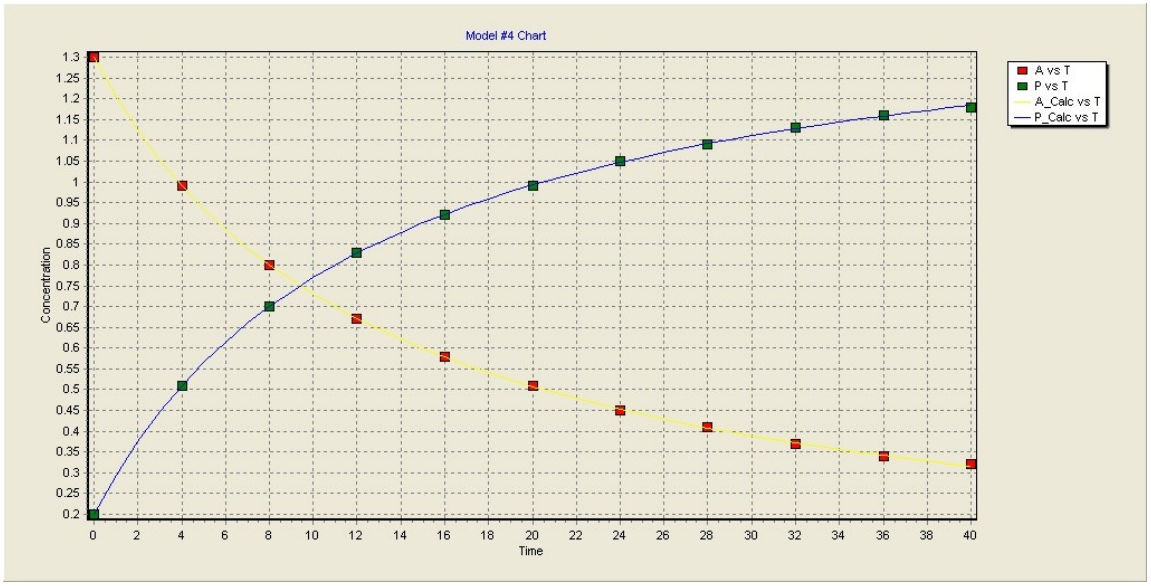
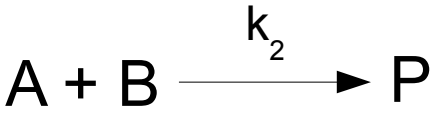


Figure 4.1 – Model #4 Second-Order Irreversible Reaction

Model #5: Second-Order Irreversible Reaction



$$A_0 \neq B_0$$

This model has several possible uses. First, it can determine the second order reaction rate, K2, given the initial concentrations of the two reagents, A0 and B0, the initial concentration of the product, P0, and a number of measurements of the reagents, A and B, and the product, P, over a time interval. It could also be used to simulate the concentration of the product, P, given the initial concentrations of A and B, A0 and B0, the initial concentration of P, P0, and a number of measurements of A and B over a period of time. Two other uses for this model are to simulate the concentration of A or B given the initial concentrations of each reagent and the product, and a number of measurements of the concentration of the other reagent and the product over a time interval. This example will demonstrate the first of these options. The model for these possible calculations is as follows:

// Model #5 - Second-Order Irreversible Reaction
// A0 Not Equal to B0

IndVars: T

DepVars: A, B, P

Params: AO, BO, PO, K2

A = AO-AO*BO*(1-EXP(K2*T*(BO-AO)))/(AO-BO*EXP(K2*T*(BO-AO)))
B = BO-AO*BO*(1-EXP(K2*T*(BO-AO)))/(AO-BO*EXP(K2*T*(BO-AO)))
P = PO+AO*BO*(1-EXP(K2*T*(BO-AO)))/(AO-BO*EXP(K2*T*(BO-AO)))

Instead of obtaining experimental measurements for the data, we perform a simulation and round the resulting numbers to two places after the decimal to produce small errors. The results of this simulation are:

T	A	B	P
0	1.5	2	0.2
2	1.06	1.56	0.64
4	0.8	1.3	0.9
6	0.63	1.13	1.07
8	0.51	1.01	1.19
10	0.42	0.92	1.28
12	0.35	0.85	1.35
14	0.3	0.8	1.4
16	0.26	0.76	1.44
18	0.22	0.72	1.48
20	0.19	0.69	1.5

The above data set was generated using some initial parameter values. Since we are not trying to prove that the answer obtained from a least squares curve fitting is the best that can be found, we will skip the simplex search which would normally be done at this time. Instead, we will start the curve fitting from the following initial parameter values:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
AO	1.5	0	INF	Y	N
BO	2	0	INF	Y	N
PO	0.2	0	INF	Y	N
K2	0.1	0	INF	N	N

For this fitting we select only K2 to be varied. The values of the other parameters should not change since they are physically measured constants rather than data we are trying to fit. The result of the least squares fitting is:

K2 = 0.099043

The sum of squared deviations at this point is 0.00014571 which is reasonably small but not overly much so. We now check to see how good the fit was by examining the statistical output which is shown below.

Data Set Name: Model #5

	Weighted	Unweighted
Sum of squared observations:	35.169	35.169
Sum of squared deviations:	0.00014571	0.00014571
Standard deviation of data:	0.0021338	0.0021338
R-squared:	1	1
Coefficient of determination:	0.99998	0.99998
Correlation:	0.99999	0.99999
Model Selection Criterion:	10.735	10.735

Confidence Intervals

Parameter Name:	K2	
Estimated Value:	0.099043	
Standard Deviation:	0.00010902	
95% Range (Univariate):	0.098821	0.099265
95% Range (Support Plane):	0.098821	0.099265

Variance-Covariance

1.1886E-008

Correlation Matrix

1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	0.31634	is probably not significant.
Skewness	8.3562	indicates the likelihood of a few large positive residuals having an unduly large effect on the fit.
Kurtosis:	3.6291	is probably not significant
Weighting Factor:	0	
Heteroscedacticity:	0.39193	
Optimal Weighting Factor:	0.39193	

The above output is probably a little better than we had expected given a sum of squared deviations as large as we have for this problem. The Model Selection Criterion is greater than ten which is quite good and the confidence limits on K2 are within 0.5% of each other which is also good considering the size of the errors in the data set. We conclude that this model is able to fit data well and obtain an error of no more than the size of the perturbations of the data. We could not ask a model to produce output that was much better. The plot of the data set and the curve which was fit to it are shown in Figure 5.1 below.

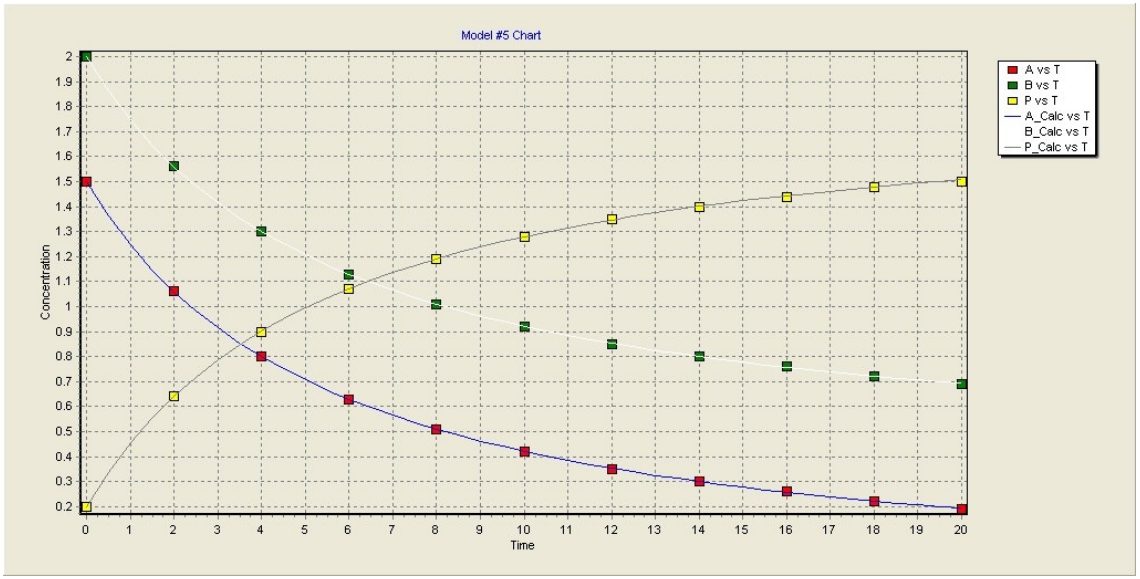
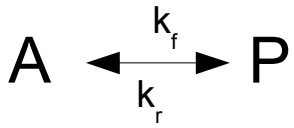


Figure 5.1 – Model #5 Second-Order Irreversible Reaction

Model #6: First-Order Reversible Reaction



There are several uses to which this model can be put. First, it can be employed to find the forward and reverse reaction rates, KF and KR, given the initial concentration of the reagent A, A0, the initial concentration of the product P, P0, and a number of measurements of the concentrations of A and P over a time interval. The second use for this model is to simulated the concentration of P given the initial concentrations of A and P, A0 and P0, and a number of measurements of the concentration of A over time. The third possible use for this model is to simulate the concentration of A given the initial concentrations of A and P, and a number of measurements of the concentration of P over a period of time. Since the first option would be the most used, we will demonstrate how to work with it in this example. The form of this model is as follows:

// Model #6 - First-Order Reversible Reaction

IndVars: T

DepVars: A, P

Params: AO, PO, KF, KR

A = (KR*(AO+PO)+(KF*AO-KR*PO)*EXP((-(KF+KR))*T))/(KF+KR)
P = (KF*(AO+PO)-(KF*AO-KR*PO)*EXP((-(KF+KR))*T))/(KF+KR)

In order to perform a curve fitting, we need some measurements of A and P over a time interval. Instead of experimentally determining these values, we will do a simulation of the model with some initial parameter values and round the data to two places after the decimal. This is reasonable for demonstration purposes since it will produce small errors. Experimental data might not be so consistently close to the actual answer, but it should not be too different from this data set. The data points generated by this method are as follows:

T	A	P
0	1.6	0.4
4	1.37	0.63
8	1.2	0.8
12	1.08	0.92
16	0.99	1.01
20	0.92	1.08
24	0.87	1.13
28	0.84	1.16
32	0.82	1.18
36	0.8	1.20
40	0.78	1.22

The values of the parameters that were used to obtain this set of data should be good enough starting points for a least squares curve fitting. This is true only for this demonstration because a simplex search is a good means of being assured that the answer that is found is the best answer in the local region of parameter space. The initial values are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
AO	1.6	0	INF	Y	N
PO	0.4	0	INF	Y	N
KF	0.05	0	INF	N	N
KR	0.03	0	INF	N	N

The least squares fitting is done with KF and KR selected for fitting since we wish to know both of these values. The best-fit values that Scientist finds are:

KF = 0.049443
KR = 0.029466

The sum of squared deviations for the last step in the fitting is 0.00018026 which is reasonably good. We cannot say more about the fit of the simulated curve to the data without looking at the statistical output that Scientist provides. This output is shown below.

Data Set Name: Model #6

	Weighted	Unweighted
Sum of squared observations:	23.426	23.426
Sum of squared deviations:	0.00018026	0.00018026
Standard deviation of data:	0.0030022	0.0030022
R-squared:	0.99999	0.99999
Coefficient of determination:	0.99987	0.99987
Correlation:	0.99994	0.99994
Model Selection Criterion:	8.7943	8.7943

Confidence Intervals

Parameter Name:	KF	
Estimated Value:	0.049443	
Standard Deviation:	0.00024065	
95% Range (Univariate):	0.048941	0.049945
95% Range (Support Plane):	0.048807	0.050079

Parameter Name:	KR	
Estimated Value:	0.029466	
Standard Deviation:	0.00024846	
95% Range (Univariate):	0.028948	0.029984
95% Range (Support Plane):	0.028809	0.030123

Variance-Covariance Matrix

5.7913E-008	
5.7442E-008	6.1734E-008

Correlation Matrix

1	
0.96069	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	0.9021	is probably not significant
Skewness	4.5241E-013	is probably not significant
Kurtosis:	-0.72217	is probably not significant
Weighting Factor:	0	
Heteroscedacticity:	-4.7889E-015	
Optimal Weighting Factor:	-4.885E-015	

The above output suggests that we did not obtain as good a fit as we would like. The Model Selection Criterion is less than nine which is good, but not overly so. We also see that the confidence limits for the parameters vary by around 1% which is about what

must be expected given that the errors in the data set can be as much as 0.5% and we are trying to fit two parameters to this slightly inaccurate data. We therefore conclude that this model produces quite reasonable output and that the numbers that we obtained for the forward and reverse reaction rates are fairly well determined. A plot of the calculated curve and the data set are shown in Figure 6.1 below.

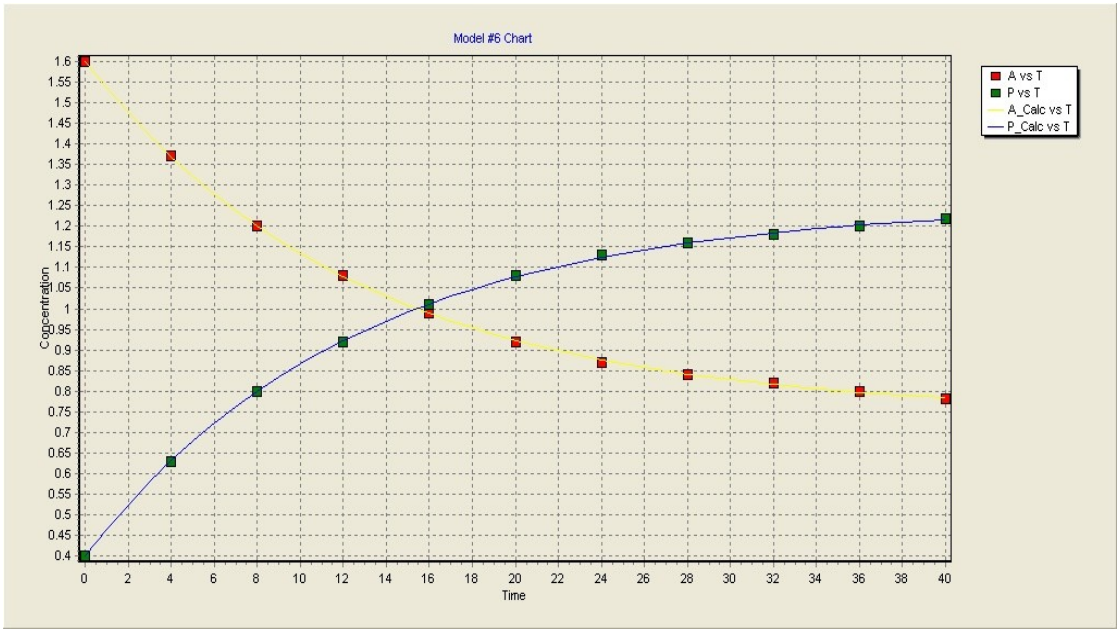


Figure 6.1 – Model #6 First-Order Reversible Reaction

Model #7: pH-Rate Profile (Nonelectrolyte)

The equation that describes the pH-rate profile for a nonelectrolyte is as follows:

$$k_{obs} = k_1 * [H^+] + k_2 + k_3 * [OH^-]$$

$$\text{where: } OH^- = K_w / H^+$$

$\mathbf{K_w}$ is the ion product for water (1.0E-14 at 25 degrees Centigrade). The model form of this equation may be used to find the rate constants, $\mathbf{k_1}$, $\mathbf{k_2}$ and $\mathbf{k_3}$, given a number of measurements of the pH and of $\mathbf{k_{obs}}$ (typically the observed first-order reaction rate). It could also be used to simulate the observed reaction rate, $\mathbf{k_{obs}}$, given values for the reaction rate constants, $\mathbf{k_1}$, $\mathbf{k_2}$ and $\mathbf{k_3}$. The model used for these purposes is as follows:

```
// Model #7 - pH-Rate Profile
// Nonelectrolyte

    IndVars:  PH

    DepVars:  KOBS

    Params:  K1, K2, K3, KW

    H = 10^(-PH)
    KOBS = K1*H+K2+K3*KW/H
```

We will now proceed with an example showing how to find the rate constants, $\mathbf{k_1}$, $\mathbf{k_2}$ and $\mathbf{k_3}$, since this will be the most typical use of this model. To do this, we need to construct a data set. We perform a simulation with some assumed parameter values and round the results to three significant digits. The data set constructed in the above manner for this example is:

PH	KOBS
0.0	2.4
0.5	0.825
1.0	0.328
1.5	0.17
2.0	0.121
3.0	0.0998
4.0	0.0977
5.0	0.0975
6.0	0.0975
7.0	0.0974
8.0	0.0975
9.0	0.098
10.0	0.103
11.0	0.151
12.0	0.635
12.5	1.80
13.0	5.47
13.5	17.1
14.0	53.8

The parameter values that were used to generate this data set will be used as the initial conditions for the least squares curve fitting. We will not refine the values with a simplex search since they should already be close enough to the final solution. The initial parameter values are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
K1	2.3	0	INF	N	N
K2	0.0975	0	INF	N	N
K3	53.7	0	INF	N	N
KW	1E-014	0	INF	Y	N

The least squares fitting with a weighting factor of 2.0 for this problem since the values in this data set vary over a number of the orders of magnitude and therefore the errors for each point are roughly proportional to the square of the inverse of its value. We fix KW for fitting since it is a constant depending on temperature and therefore should not vary for this problem. We now perform the least squares fitting and obtain the following results:

K1 = 2.3024
K2 = 0.097498
K3 = 53.749

The sum of squared deviation for this fit is 2.9342E-5 which is quite good. We now check the rest of the statistical output that Scientist provides in order to see if they indicate they we obtained as good a fit as the sum of squared deviations implies. The statistics for this model are shown below.

Data Set Name: Model #7

	Weighted	Unweighted
Sum of squared observations:	19	3227.1
Sum of squared deviations:	2.9342E-005	0.002205
Standard deviation of data:	0.0013542	0.011739
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	12.51	13.76

Confidence Intervals

Parameter Name:	K1	
Estimated Value:	2.3024	
Standard Deviation:	0.002035	
95% Range (Univariate):	2.298	2.3067
95% Range (Support Plane):	2.296	2.3087

Parameter Name:	K2	
Estimated Value:	0.097498	
Standard Deviation:	4.3858E-005	
95% Range (Univariate):	0.097405	0.097591
95% Range (Support Plane):	0.097362	0.097635

Parameter Name:	K3	
Estimated Value:	53.749	
Standard Deviation:	0.033708	
95% Range (Univariate):	53.678	53.82
95% Range (Support Plane):	53.644	53.854

Variance-Covariance Matrix

4.1413E-006		
-1.4614E-008	1.9235E-009	
8.4427E-007	-1.1112E-007	0.0011362

Correlation Matrix

1		
-0.16374	1	
0.012308	-0.075167	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation	-1.729	is probably not significant.
Skewness	-5.9646	indicates the likelihood of a few large negative residuals having an unduly large effect on the fit.
Kurtosis	4.2516	is probably not significant.
Weighting Factor:	2	
Heteroscedacticity	-0.063766	
Optimal Weighting Factor	1.9362	

These figures show us that we did obtain a good fit. The Model Selection Criterion is larger than ten and the confidence limits do not deviate very much from the calculated values. Also, the relatively small off diagonal terms in the variance-covariance matrix and the correlation matrix show that the parameter values are independently

determined as we would hope. Although some of the statistics are better for the unweighted case, we accept the weighted values because they better represent the errors in the data. We decide that the fit is good enough for this demonstration and draw the plot of the pH versus the log of the observed reaction rate. This plot is shown in Figure 7.1 below.

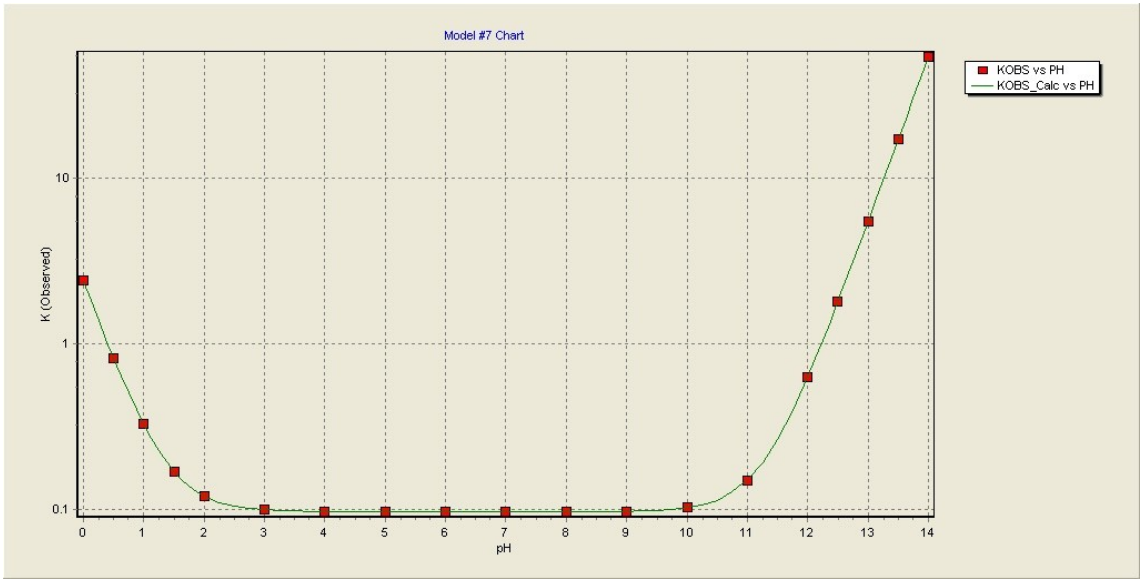


Figure 7.1 – Model #7 pH-Rate Profile (Nonelectolyte)

Model #8: pH-Rate Profile (Monoprotic Acid)

The equation that describes the pH-rate profile for a monoprotic acid is as follows:

$$k_{obs} = k_1 * [H^+] * f_{HA} + k_2 * f_{HA} + k_3 * f_{A^-} + k_4 * [OH^-] * f_{A^-}$$

where: $f_{HA} = H^+ / (H^+ + K_a)$

$$f_{A^-} = K_a / (H^+ + K_a)$$

$$OH^- = K_w / H^+$$

In the above equations, $\mathbf{K_w}$ is the ion product of water (1.0E-14 at 25 degrees Centigrade) and $\mathbf{K_a}$ is the acid ionization constant. This set of equations in model form may be used to find the reaction rate constants, k1, k2, k3 and k4, given a number of measurements of kobs (typically the first-order observed reaction rate) over a set of values of pH. This model can also be used to find the acid ionization constant, Ka, given the reaction rate constants, k1, k2, k3 and k4, and the measurements of kobs versus pH. The model form of the above equations is as follows:

// Model #8 - pH-Rate Profile
// Monoprotic Acid

IndVars: PH

DepVars: KOBS

Params: K1, K2, K3, K4, KA, KW

```
H = 10^(-PH)
FHA = H/(H+KA)
FA = KA/(H+KA)
KOBS = K1*H*FHA+K2*FHA+K3*FA+K4*KW*FA/H
```

In order to perform the least squares curve fitting to determine the rate constants, k1, k2, k3, and k4, we need to have a set of measurements of kobs over a range of pH. The data set which is obtained by performing a simulation with set values of the parameters is shown below.

PH	KOBS
0.0	6.49
0.5	2.19
1.0	0.825
1.5	0.394
2.0	0.258
3.0	0.201
4.0	0.196
5.0	0.195
6.0	0.197
7.0	0.217
8.0	0.415
9.0	2.21
10.0	11.3
11.0	20.4
12.0	22.5
12.5	23.4
13.0	25.6
13.5	32.7
14.0	55.1

Because the data set was generated from given parameter values, we will use these figures to begin the least squares fitting. The simplex search is omitted because it will not make much difference in finding better starting values. The parameters used to generate the data set are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
K1	6.3	0	INF	N	N
K2	0.195	0	INF	N	N
K3	22.4	0	INF	N	N
K4	32.7	0	INF	N	N
KA	1E-010	0	INF	Y	N
KW	1E-014	0	INF	Y	N

The curve fitting will be performed with a weighting factor of 2.0 since the data is rounded to three decimal places corresponding to an error roughly proportional to the inverse of the square of the value. We fix KA and KW for fitting since they should not vary for this fit. The least squares fitting yields the following results:

K1 = 6.3012
K2 = 0.19489
K3 = 22.393
K4 = 32.688

The sum of squared deviations for the fit is 1.9223E-5 which is quite good. We now look at the statistical output to determine just how good the fit was. This output is as follows:

Data Set Name: Model #8

	Weighted	Unweighted
Sum of squared observations:	19	6411.4
Sum of squared deviations:	1.9223E-005	0.0046027
Standard deviation of data:	0.0011321	0.017517
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	13.573	13.304

Confidence Intervals

Parameter Name:	K1	
Estimated Value:	6.3012	
Standard Deviation:	0.0044491	
95% Range (Univariate):	6.2917	6.3106
95% Range (Support Plane):	6.2856	6.3167

Parameter Name:	K2		
Estimated Value:	0.19489		
Standard Deviation:	9.3535E-005		
95% Range (Univariate):	0.19469	0.19509	
95% Range (Support Plane):	0.19457	0.19522	

Parameter Name:	K3		
Estimated Value:	22.393		
Standard Deviation:	0.010779		
95% Range (Univariate):	22.37	22.416	
95% Range (Support Plane):	22.355	22.43	

Parameter Name:	K4		
Estimated Value:	32.688		
Standard Deviation:	0.057899		
95% Range (Univariate):	32.564	32.811	
95% Range (Support Plane):	32.485	32.89	

Variance-Covariance Matrix

1.9795E-005			
-8.0418E-008		8.7488E-009	
7.2514E-007	-	7.8892E-008	0.00011618
-1.4106E-006		1.5347E-007	-0.00022604

Correlation Matrix

1			
-0.19324	1		
0.015121	-0.078253	1	
-0.005476	0.028338	-0.3622	

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-2.1054	is probably not significant.
Skewness	-3.0168	indicates the likelihood of a few large negative residuals having an unduly large effect on the fit.
Kurtosis	0.29276	is probably not significant.
Weighting Factor:	2	
Heteroscedacticity:	-0.078134	
Optimal Weighting Factor:	1.9219	

The above statistics indicate that we obtained an excellent fit of the simulated curve to the data points. In particular, the Model Selection Criterion is greater than 13 and the confidence limits on the parameter values are very good. The variance-covariance and correlation matrices do not indicate as much independence of parameters as was found for Model #7, but we are confident that the simulated curve fits the data so we plot the results. This plot is shown in Figure 8.1.

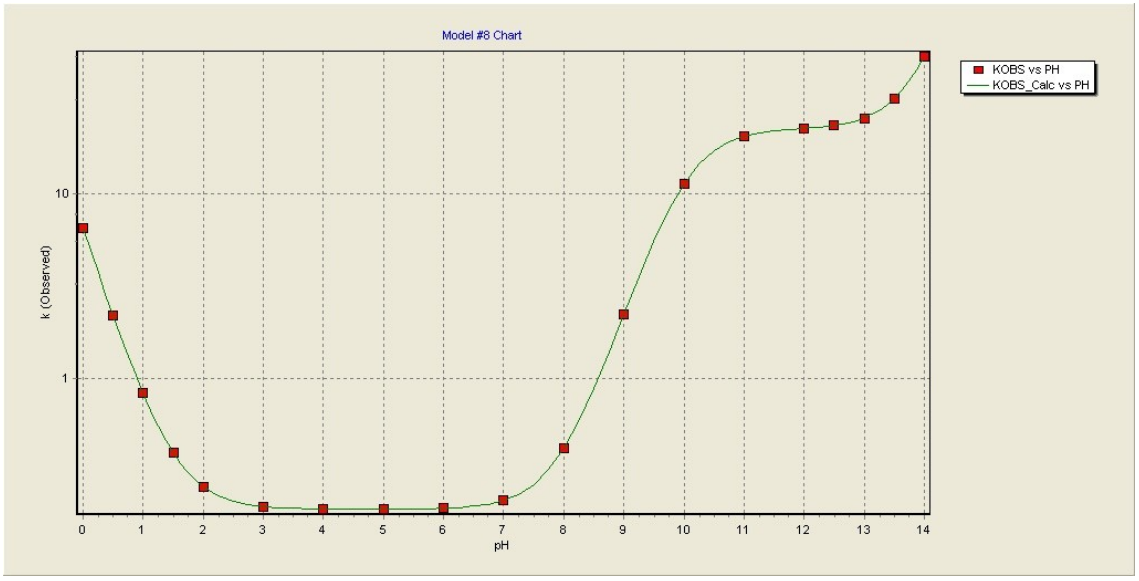


Figure 8.1 - Plot for pH-Rate Profile (Monoprotic Acid)

Model #9: pH-Rate Profile (Diprotic Acid)

The equation describing the pH-rate profile for a diprotic acid is as follows:

kobs = k1 * [H+] * fH2A + k2 * fH2A + k3 * fHA- + k4 * fA- + k5 * [OH-] * fA-

Where: fH2A = H+ ^ 2 /(H+ ^ 2 + Ka1 * H+ + Ka1 * Ka2)

fHA- = Ka1 * H+ / (H+ ^ 2 + Ka1 * H+ + Ka1 * Ka2)

fA- = Ka1 * Ka2 / (H+ ^ 2 + Ka1 * H+ + Ka1 * Ka2)

OH- = Kw / H+

In the above equations, Kw is the ion product of water (1.0E-14 at 25 degrees Centigrade) and Ka1 and Ka2 are the acid ionization constants. The model form of these equations is normally used to find the rate constants, k1, k2, k3, k4 and k5, given measurements of kobs (typically the first-order observed reaction rate) over a range of pH. It may also be used to find the acid ionization constants given values for the rate constants, k1, k2, k3, k4 and k5, and the measurements of pH versus kobs. Since the first use of the model is more typical, we will perform that calculation in this example. The model form of the equations is:

// Model #9 - pH-Rate Profile
// Diprotic Acid

IndVars: PH

DepVars: KOBS

Params: K1, K2, K3, K4, K5, KA1, KA2, KW

H = 10^(-PH)
FH2A = H^2/(H^2+KA1*H+KA1*KA2)
FHA = KA1*H/(H^2+KA1*H+KA1*KA2)
FA = KA1*KA2/(H^2+KA1*H+KA1*KA2)
KOBS = K1*H*FH2A+K2*FH2A+K3*FHA+K4*FA+K5*KW*FA/H

To begin the curve fitting process, we need some measurements of KOBS over a range of PH. We obtain data of this sort by performing a simulation of the model over a range of PH given set values for the parameters. This data set is as follows:

PH	KOBS
0.0	53.7
0.5	39.1
1.0	34.5
1.5	33.1
2.0	32.6
3.0	32.4
4.0	32.4
5.0	32.4
6.0	32.4
7.0	32.3
8.0	32.1
9.0	29.8
10.0	18.2
11.0	6.61
12.0	4.08
12.5	3.96
13.0	7.04
13.5	24.8
14.0	90.1

The parameter values used to generate this data set will also be used as the initial guesses to begin the least squares fitting. We will not do a simplex search since the values should be close enough to the least squares solution for demonstration purposes. The initial parameter values are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
K1	21.3	0	INF	N	N
K2	32.4	0	INF	N	N
K3	4.1	0	INF	N	N
K4	0.1	0	INF	N	N
K5	98.6	0	INF	N	N
KA1	1E-010	0	INF	Y	N
KA2	1E-013	0	INF	Y	N
KW	1E-014	0	INF	Y	N

We now fix, KA2, and KW for fitting since we do not want them to vary for this problem. A weighting factor of 2.0 will be used in fitting this data since the errors are roughly proportional to the inverse of the squares of the values. Problems where the data values varied over several orders of magnitude are more accurately fitted with a weighting factor of 2.0. We start the least squares fitting and find that the best fit values are:

K1 = 21.313
K2 = 32.379
K3 = 4.0968
K4 = 0.10885
K5 = 98.650

The sum of squared deviations at this point is 1.2894E-5 which is good. We now examine the statistical summary shown below to see if the fit is as good as the sum of squared deviations indicates.

Data Set Name: Model #9

	Weighted	Unweighted
Sum of squared observations:	19	24112
Sum of squared deviations:	1.2894E-005	0.0115
Standard deviation of data:	0.0009597	0.028661
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	13.871	12.781

Confidence Intervals

Parameter Name:	K1	
Estimated Value:	21.313	
Standard Deviation:	0.049208	
95% Range (Univariate):	21.207	21.418
95% Range (Support Plane):	21.123	21.502

Parameter Name:	K2	
Estimated Value:	32.379	
Standard Deviation:	0.0095833	
95% Range (Univariate):	32.358	32.399
95% Range (Support Plane):	32.342	32.415

Parameter Name: K3
Estimated Value: 4.0968
Standard Deviation: 0.0041957
95% Range (Univariate): 4.0878 4.1058
95% Range (Support Plane): 4.0807 4.1129

Parameter Name: K4
Estimated Value: 0.10885
Standard Deviation: 0.017461
95% Range (Univariate): 0.071404 0.1463
95% Range (Support Plane): 0.0417 0.17601

Parameter Name: K5
Estimated Value: 98.65
Standard Deviation: 0.085807
95% Range (Univariate): 98.466 98.834
95% Range (Support Plane): 98.32 98.98

Variance-Covariance

0.0024214				
-0.00014747	9.1839E-005			
8.3624E-006	-5.2079E-006	1.7604E-005		
-2.2182E-005	1.3814E-005	-5.1792E-005	0.00030489	
5.7916E-005	-3.6068E-005	0.00014011	-0.001037	0.0073628

Correlation Matrix

1				
-0.31272	1			
0.040504	-0.12952	1		
-0.025817	0.082556	-0.70695	1	
0.013717	-0.043863	0.38918	-0.69215	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-1.1861	is probably not significant.
Skewness	1.037	indicates the likelihood of a few large positive residuals having an unduly large effect on the fit.
Kurtosis	-0.24815	is probably not significant.
Weighting Factor:	2	
Heteroscedacticity:	0.72776	
Optimal Weighting Factor:	2.7278	

The Model Selection Criterion indicates that we obtained a good fit of the simulated curve to the data set. However, the confidence limits were not as good as might be desired especially for K4. An MSC of 13 or more is very good, but the confidence limits for the parameters were not very well determined. We feel, however, that the fit is good enough for this example so we plot the results. This plot is shown in Figure 9.1 below.

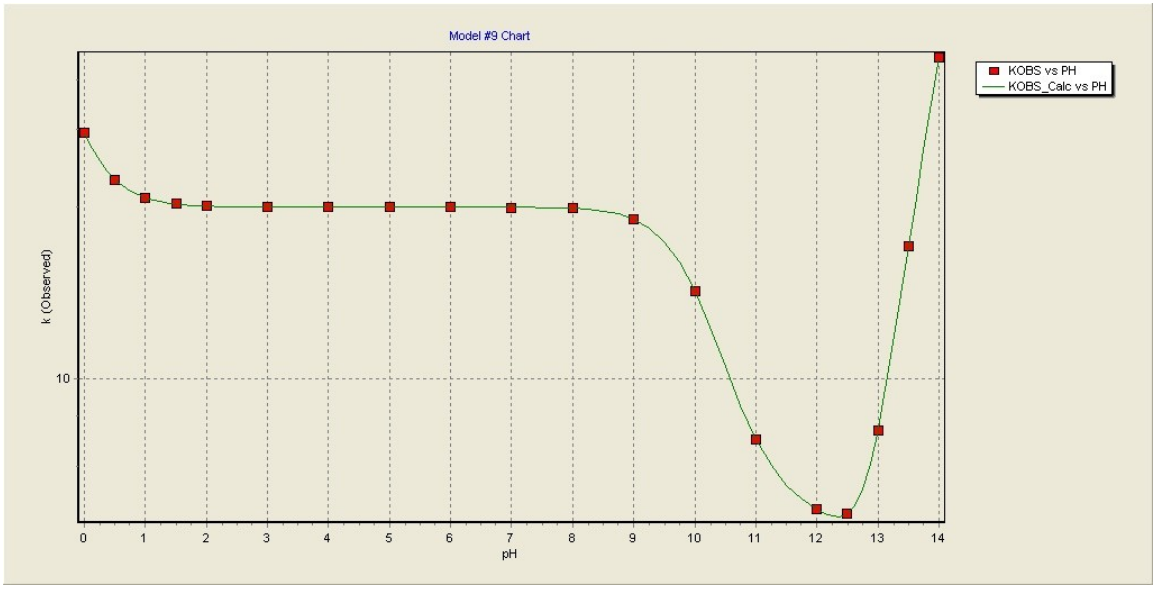


Figure 9.1 – Model #9 pH-Rate Profile (Diprotic Acid)

Model #10: Arrhenius Equation (Linearized Form)

The Arrhenius Equation as shown below allows the activation energy to be found from the temperature dependence of the reaction rate. It is possible with the Scientist model constructed from this equation to find the parameters A and Ea which determine the reaction rate. Ea is given in units of calories/mole.

$$k = A * e^{\frac{-Ea}{(R*T)}}$$

With this model, the best-fit values of the parameters A and EA can be found given a number of measurements of the reaction rate and the inverse of the temperature measured in degrees Kelvin. The last condition is necessary to obtain linear graphics. To obtain nonlinear graphics, use Model #11. This model could also be used to simulate the reaction rate given values of the parameters A and EA. Since the determination of A and EA will be the most common use for this model, this example will deal with the method used to obtain values for these parameters. The model form of this equation is shown below.

// Model #10 - Arrehnius Equation
// Linearized Form

IndVars: TINV

DepVars: K

Params: A, EA

K = A*EXP((-EA)*TINV/1.987)

As with any least squares fitting, this example requires a set of data points. The set used here was obtained by performing a simulation with some initial parameter values and the rounding the resulting data to produce small errors. The data that was obtained by this method is as follows:

TINV	K
0.0027	8.06E-006
0.0028	4.64E-006
0.0029	2.66E-006
0.003	1.53E-006
0.0031	8.81E-007
0.0032	5.06E-007
0.0033	2.91E-007
0.0034	1.67E-007
0.0035	9.62E-008
0.0036	5.53E-008

The initial parameters will be close enough to the solution for this demonstration so we will not perform a simplex search. This is not the ideal method for finding the best solution but it is adequate for this example. The starting values of the parameters are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
A	25	0	INF	N	N
EA	11000	0	INF	N	N

The least squares fitting is done with both parameters selected to be fit and the weighting factor set to 2.0. The weighting factor is set in this manner because the errors in the data set calculated are roughly proportional to the square of the inverse of the magnitude of the data point. The results of this calculation are as follows:

A = 24.989
EA = 11000

The sum of squared deviations for this fit was 8.0410E-6 which is good. The statistical output for this model is shown below.

Data Set Name: **Model #10**

	Weighted	Unweighted
Sum of squared observations:	10	9.7067E-011
Sum of squared deviations:	8.041E-006	6.0172E-017
Standard deviation of data:	0.0010026	2.7425E-009
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	14.176	13.436

Confidence Intervals

Parameter Name:	A		
Estimated Value:	24.989		
Standard Deviation:	0.088018		
95% Range (Univariate):		24.786	25.192
95% Range (Support Plane):		24.727	25.252

Parameter Name:	EA		
Estimated Value:	11000		
Standard Deviation:	2.2323		
95% Range (Univariate):		10995	11005
95% Range (Support Plane):		10993	11007

Variance-Covariance Matrix

0.0077471	
0.19568	4.9831

Correlation Matrix

1	
0.99594	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-0.92828	is probably not significant.
Skewness	0.6995	is probably not significant.
Kurtosis:	0.41513	is probably not significant.
Weighting Factor:	2	
Heteroscedacticity:	4.7156E-008	
Optimal Weighting Factor:	2	

It is reassuring to note that the fit for the weighted data is much better than the unweighted fit. The Model Selection Criterion is quite high indicating a rather good fit of the calculated curve to the data even though the confidence limits for the parameters were somewhat wider than is desirable. If we were attempting to find accurate results instead of demonstrating the method by which they may be obtained, we would find a more accurate data set, but we will not do so here. The plot for this fit is obtained by plotting K logarithmically. The plot is shown in Figure 10.1 below.

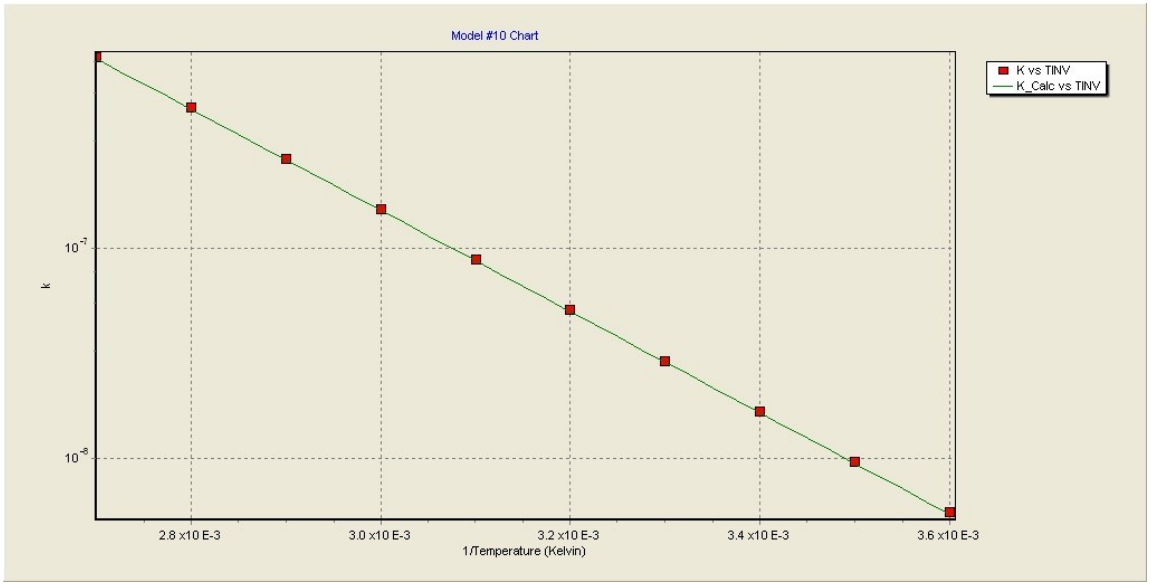


Figure 10.1 – Model #10 Arrhenius Equation (Linearized Form)

Model #11: Arrhenius Equation (Nonlinear Form)

As with Model #10, this model may be used to find the parameters A and Ea for the following equation where Ea is given in units of calories/mole:

$$k = A * e^{\frac{-Ea}{(R*T)}}$$

These parameters can be found given a number of measurements of the temperature in degrees Celsius and the reaction rate. This model could also be used to simulate the reaction rate given known values of the parameters, but finding the values of A and Ea is more common so we will find them as a demonstration of this model. The form that the above equation takes in Scientist is as follows:

// Model #11 - Arrhenius Equation
// Non-Linear Form

IndVars: T

DepVars: K

Params: A, EA

K = A*EXP((-EA)/(1.987*(T+273)))

The data set used for this fitting was found by doing a simulation with some initial parameter values and rounding the results to three decimal places. By doing this, we create errors which are roughly proportional to the square of the inverse of the magnitude of the number. We will use this fact later when we fit the data. The data set for this case is:

T	K
5.0	8.09E-009
15.0	1.72E-008
25.0	3.48E-008
35.0	6.71E-008
45.0	1.24E-007
55.0	2.22E-007
65.0	3.82E-007
75.0	6.39E-007
85.0	1.04E-006
95.0	1.64E-006

The parameter values that were used to construct this data set are as follows:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
A	22	0	INF	N	N
EA	12000	0	INF	N	N

We will not perform a simplex search to find better starting parameters since the data was generated from these values and we are not attempting to prove that the results we get are the best that can be found. We set the weighting factor to 2.0 because the data set was constructed to have errors inversely proportional to the square of the magnitude of each value. We then do the least squares curve fitting with both A and EA selected for fitting . The results of this fit are as follows:

A = 21.974
EA = 11999

The sum of squared deviations for this fit is 1.5979E-5 which is quite good. We now examine the statistical output for this fit, looking particularly at the difference between the weighted and unweighted statistical values.

Data Set Name: **Model #11**

	Weighted	Unweighted
Sum of squared observations:	10	4.3962E-012
Sum of squared deviations:	1.5979E-005	6.9853E-018
Standard deviation of data:	0.0014133	9.3443E-010
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	13.794	12.448

Confidence Intervals

Parameter Name:	A	
Estimated Value:	21.974	
Standard Deviation:	0.11093	
95% Range (Univariate):	21.718	22.23
95% Range (Support Plane):	21.643	22.305

Parameter Name:	EA	
Estimated Value:	11999	
Standard Deviation:	3.2321	
95% Range (Univariate):	11992	12007
95% Range (Support Plane):	11990	12009

Variance-Covariance Matrix

0.012306	
0.35713	10.447

Correlation Matrix

1	
0.99607	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-0.80002	is probably not significant
Skewness	0.66904	is probably not significant
Kurtosis:	0.58966	is probably not significant
Weighting Factor:	2	
Heteroscedacticity:	1.3922E-008	
Optimal Weighting Factor:	2	

We find that the fit for the weighted case is better than that for the unweighted case. Although the Model Selection Criterion is greater than twelve for the unweighted fit, the MSC for the weighted fit is almost fourteen which is excellent. The confidence limits for these parameters are also good, but they could have been better. Since the fit is so good, we accept the resulting values of A and EA. The plot of the calculated curve and the data points is shown in Figure 11.1 below.

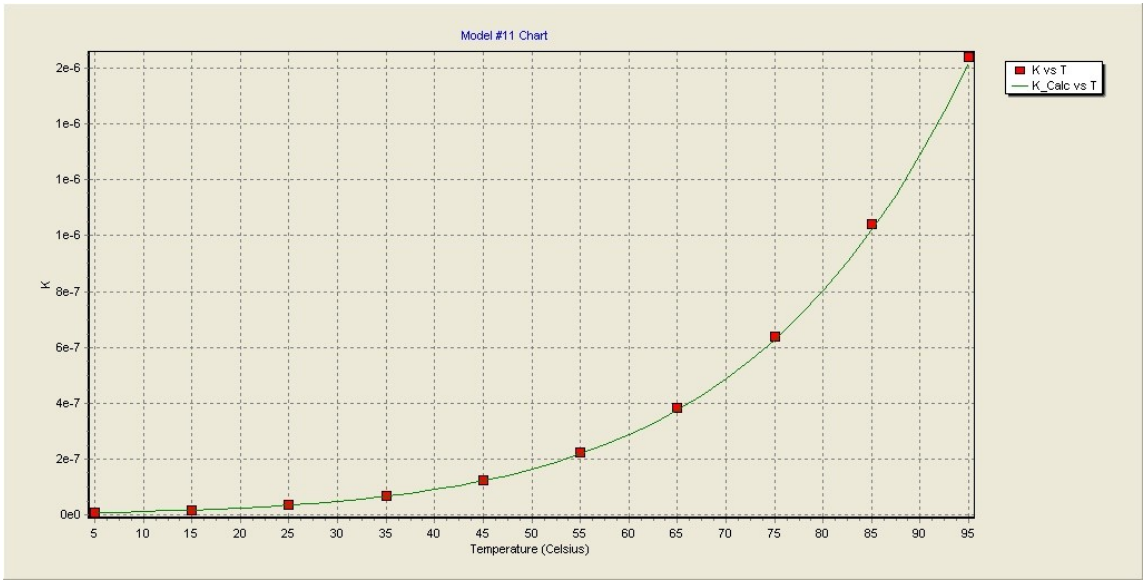


Figure 11.1 – Model #11 Arrhenius Equation (Nonlinear Form)

Model #12: Eyring Equation (Linearized Form)

The manipulations done with this model are based on the following equation:

$$k = \frac{(K * T)}{h} * e^{\frac{(\Delta S)}{R}} * e^{\frac{(\Delta H)}{(R * T)}}$$

Where K = Boltzmann's Constant
h = Plank's Constant

The model may be use to find the best fit values of the activation entropy, ΔS, and the activation enthalpy, ΔH, for the linear graphics case given a number of measurements of the inverse of the temperature in degrees Kelvin and the reaction rate divided by the temperature. It could also be used to find the entropy or enthalpy given a set value for the other parameter, but we will not perform this calculation for this example. The activation entropy is reported in units of calories/(degree * mole) and the activation enthalpy is in units of calories/mole. To find the values of these parameters for the nonlinear graphics case, use Model #13. The form that the above equation takes in Scientist is as follows:

// Model #12 - Eyring Equation
// Linearized Form

IndVars: TINV

DepVars: KDIVT

Params: S, H

KDIVT = 1.3805E-16*EXP(S/1.987)*EXP((-H)*TINV/1.987)/6.6255E-27

The data set to be used for this demonstration was generated by performing a simulation with set values of the parameters and rounding the resulting figures to three decimal places. This produces small errors in each data point which approximate experimental measurements. This data set is:

TINV	KDIVT
0.0027	43300.0
0.0028	26200.0
0.0029	15800.0
0.0030	9560.0
0.0031	5780.0
0.0032	3490.0
0.0033	2110.0
0.0034	1280.0
0.0035	772.0
0.0036	467.0

The initial parameter values to be used for curve fitting will be the values used to generate the data set. These values are as follows:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
S	1.0	0	INF	N	N
H	10000	0	INF	N	N

The least squares fitting will be performed directly without being preceded by a simplex search since the data was generated from the initial parameter values. For this fitting, we will use a weighting factor of 2.0 since we have rounded numbers which vary over a large range to three significant digits. The effect of this rounding is to produce errors which are roughly proportional to the inverse of the square of the magnitude of the value and thus the weighting factor of 2.0. We perform the least squares fit and find that the best fit values of the activation entropy and enthalpy are:

S = 1.0014
H = 10000

We also find a sum of squared deviations of 1.1802E-5 which is fairly good. To see whether the fit of the calculated curve to the data is good enough, we look at the statistical summary that Scientist calculates. These statistics are shown below.

Data Set Name: **Model #12**

	Weighted	Unweighted
Sum of squared observations:	10	2.9549E009
Sum of squared deviations:	1.1802E-005	2079.1
Standard deviation of data:	0.0012146	16.121
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	13.653	13.256

Confidence Intervals

Parameter Name:	S		
Estimated Value:	1.0014		
Standard Deviation:	0.0084717		
95% Range (Univariate):	0.98186	1.0209	
95% Range (Support Plane):	0.9761	1.0267	

Parameter Name:	H		
Estimated Value:	10000		
Standard Deviation:	2.7006		
95% Range (Univariate):	9993.9	10006	
95% Range (Support Plane):	9992.1	10008	

Variance-Covariance Matrix

7.177E-005	
0.022786	7.2935

Correlation Matrix

1	
0.99594	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-0.4249	is probably not significant
Skewness	-1.2081	indicates the likelihood of a few large negative residuals having an unduly large effect on the fit.
Kurtosis:	-0.11959	is probably not significant
Weighting Factor:	2	
Heteroscedacticity:	184.71	
Optimal Weighting Factor:	186.71	

While studying these statistics, we find two things which are noteworthy. First, the confidence limits for S are not as good as they could be. And second, the Model Selection Criterion for the weighted case is marginally better than that for the unweighted case. This would suggest that by using a weighting factor of 0.0 we could produce roughly the same results. However, a weighting factor of 0.0 means that only the first few points of this data set is significant since the data following it is one to two magnitudes smaller. Weighting the data in this manner means that we essential ignore all but the first two or three points. This is not what we would like to have. Therefore, we find that the results for the weighted case are much more meaningful.

In order to obtain a linear graphics plot of the calculated curve and the data set, it is necessary to specify a logarithmic axis for the dependent variable. This plot is shown in Figure 12.1 below.

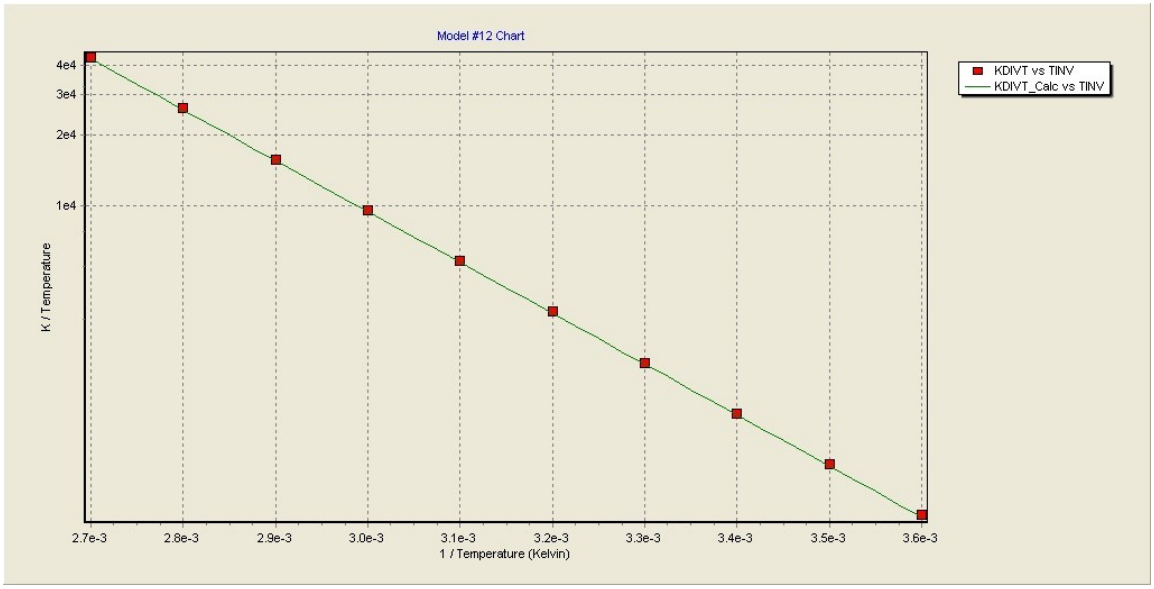


Figure 12.1 – Model #12 Eyring Equation (Linearized Form)

Model #13: Eyring Equation (Nonlinear Form)

As in Model #12, this model is represented by the following equation:

$$k = \frac{(K * T)}{h} * e^{\frac{(\Delta S)}{R}} * e^{\frac{(\Delta H)}{(R * T)}}$$

Where K = Boltzmann's Constant
h = Plank's Constant

It may be used to compute the best fit values of the activation entropy, ΔS, and the activation enthalpy, ΔH, for the case of nonlinear graphics given a number of measurements of the temperature in degrees Celsius and the reaction rate. As in the discussion of the previous model, this model can be use to find the value of either the activation entropy or enthalpy given the value of the other parameter and the measurements listed above. The units for the activation entropy and enthalpy are calories/(degree * mole) and calories/mole respectively. The above equation takes on the following form in Scientist:

// Model #13 - Eyring Equation
// Nonlinear Form

IndVars: T

DepVars: K

Params: S, H

K = 1.3805E-16*(T+273)*EXP(S/1.987)*EXP((-H)/(1.987*(273+T)))/6.6255E-27

The data set used for this fitting is produced by doing a simulation with some initial parameter values and rounding the resulting figures to three decimal places. This data set is as follows:

T	K
5.0	2.79
15.0	7.90
25.0	20.9
35.0	51.9
45.0	122
55.0	272
65.0	580
75.0	1180
85.0	2330
95.0	4410

The parameter values used to generate the above data set are as follows:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
S	1.2	0	INF	N	N
H	16000	0	INF	N	N

The above figures will also be used as the starting parameter values for the least squares curve fitting. We will not perform a simplex search for this parameter values since the data was generated from them and we are only attempting to demonstrate the use of this model and not to confirm results with it. We use a weighting factor of 2.0 for the same reasons that it was used in Model #12. For this example, we also deselect S as a linear parameter in the hope of obtaining better results. The least squares fitting produces the following results:

S = 1.2008
H = 16001

The sum of squared deviations for this fit is 2.0239E-5 which is very good. In order to see just how good this fit is, we must look at the statistical output which is shown below.

Data Set Name: **Model #13**

	Weighted	Unweighted
Sum of squared observations:	10	2.6698E007
Sum of squared deviations:	2.0239E-005	76.858
Standard deviation of data:	0.0015906	3.0996
R-squared:	1	1
Coefficient of determination:	1	1
Correlation:	1	1
Model Selection Criterion:	13.985	11.999

Confidence Intervals

Parameter Name:	S	
Estimated Value:	1.2008	
Standard Deviation:	0.011323	
95% Range (Univariate):	1.1747	1.2269
95% Range (Support Plane):	1.167	1.2346

Parameter Name:	H	
Estimated Value:	16001	
Standard Deviation:	3.6611	
95% Range (Univariate):	15992	16009
95% Range (Support Plane):	15990	16011

Variance-Covariance Matrix

0.00012821	
0.041293	13.404

Correlation Matrix

1	
0.9961	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	-0.67763	is probably not significant.
Skewness	2.851	indicates the likelihood of a few large positive residuals having an unduly large effect on the fit.
Kurtosis:	2.0105	is probably not significant
Weighting Factor:	2	
Heteroscedacticity:	5.1927	
Optimal Weighting Factor:	7.1927	

It is noteworthy that the results for the weighted case are much better than those for the unweighted case, and that they are more meaningful in that all but the last few points of the data set are essentially ignored for the unweighted case since the errors were assumed to be equal. This assumption is not true and therefore the weighting factor of 2.0 produces more significant results.

The fit for this case is very good. The Model Selection Criterion is almost fourteen which is excellent and the confidence limits are good. We find that these values are acceptable and plot the calculated curve and data points. This plot is shown in Figure 13.1 below.

One additional item that is useful to note is that this model produced results that were approximately as accurate as the results of Model #12. Since both models used data sets with the same number of significant digits, either of them could be used with to obtain the best fit solution for this problem.

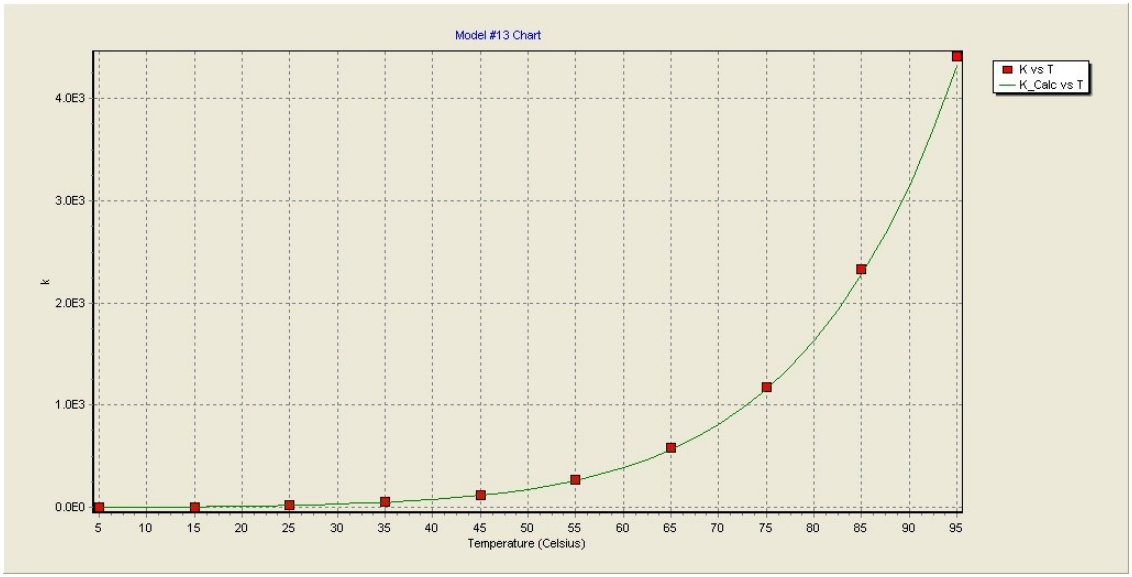
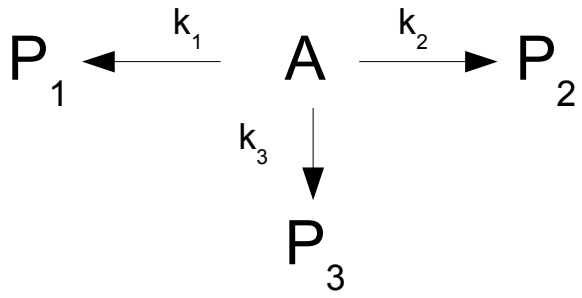


Figure 13.1 – Model #13 Eyring Equation (Nonlinear Form)

Model #14: Parallel First-Order Irreversible Reactions



This model has many possible uses. It may be used to find the reaction rates, K1, K2 and K3, given the initial concentration of the reagent A, the initial concentrations of the products P1, P2 and P3, and a number of measurements of the concentrations of the reagent and the products over a period of time. It may also be used to simulated the concentration of any one of the products given the initial concentrations of each of the products, P10, P20 and P30, the initial concentration of the reagent, A0, and a number of measurements of the concentrations of the reagent and the products other than the one being simulated over some time interval. The model can also simulate the concentration of A given the initial concentrations of A, P1, P2 and P3, and some values of the concentrations of the products measured over a period of time. This model can further be used to perform functions similar to the ones listed above for the case of two products by setting K3 and P30 to zero and deselecting them from all calculations. For this example, we will find the reaction rates for the three product case since this is probably the most common use of the model. The model that can be used for the above mentioned procedures is as follows:

// Model #14 - Parallel First-Order Irreversible Reactions

IndVars: T

DepVars: A, P1, P2, P3

Params: P1O, P2O, P3O, AO, K1, K2, K3

T1 = EXP((-(K1+K2+K3))*T)
A = AO*T1
P1 = P1O+K1*AO*(1-T1)/(K1+K2+K3)
P2 = P2O+K2*AO*(1-T1)/(K1+K2+K3)
P3 = P3O+K3*AO*(1-T1)/(K1+K2+K3)

The model shown above requires a data set for least squares curve fitting. We obtain this model by performing a simulation with some initial parameter values and rounding the results to two places after the decimal in order to produce errors comparable to those from experimental measurements. Since we are attempting to find the reaction rates, we need measurements of each of the dependent variables in order to obtain the best fit possible. The data set that is generated for this purpose is as follows:

T	A	P1	P2	P3
0.0	3	1	1.4	0.3
2.0	2.46	1.16	1.51	0.57
4.0	2.01	1.3	1.6	0.79
6.0	1.65	1.41	1.67	0.98
8.0	1.35	1.5	1.73	1.13
10.0	1.1	1.57	1.78	1.25
12.0	0.9	1.63	1.82	1.35
14.0	0.74	1.68	1.85	1.43
16.0	0.61	1.72	1.88	1.5
18.0	0.5	1.75	1.9	1.55
20.0	0.41	1.78	1.92	1.6

We will begin our curve fitting from the parameter values that were used to construct the data set. We omit the use of the simplex search because we only wish to demonstrate the method by which results may be obtained rather than trying to confirm

these results. The initial parameter values that we will use are:

Parameters

Name	Value	Lower Limit	Upper Limit	Fixed?	Linear Factorization?
P1O	1	0	INF	Y	N
P2O	1.4	0	INF	Y	N
P3O	0.3	0	INF	Y	N
AO	3	0	INF	Y	N
K1	0.03	0	INF	N	N
K2	0.02	0	INF	N	N
K3	0.05	0	INF	N	N

Given these values, we fix A0, P10, P20, and P30 since these values should remain constant and perform a least squares fit for K1, K2 and K3. The result of this fit are as follows:

K1 = 0.030026
K2 = 0.019959
K3 = 0.050007

We also find that the current sum of squared deviation for this fit is 0.00026357 which is not too bad considering the size of the errors in the data set. We now check the statistical output of Scientist to determine just how well the simulated curve fits the data set. The statistics are shown below.

Data Set Name: Model #14

	Weighted	Unweighted
Sum of squared observations:	101.64	101.64
Sum of squared deviations:	0.00026357	0.00026357
Standard deviation of data:	0.0025355	0.0025355
R-squared:	1	1
Coefficient of determination:	0.99998	0.99998
Correlation:	0.99999	0.99999
Model Selection Criterion:	10.604	10.604

Confidence Intervals

Parameter Name:	K1	
Estimated Value:	0.030026	
Standard Deviation:	4.0953E-005	
95% Range (Univariate):	0.029943	0.030108
95% Range (Support Plane):	0.029906	0.030145

Parameter Name:	K2	
Estimated Value:	0.019959	
Standard Deviation:	3.8846E-005	
95% Range (Univariate):	0.019881	0.020038
95% Range (Support Plane):	0.019846	0.020072

Parameter Name:	K3	
Estimated Value:	0.050007	
Standard Deviation:	4.5867E-005	
95% Range (Univariate):	0.049915	0.0501
95% Range (Support Plane):	0.049874	0.050141

Variance-Covariance Matrix

1.6772E-009		
-1.2173E-010	1.509E-009	
1.5236E-010	2.9478E-011	2.1038E-009

Correlation Matrix

1		
-0.076517	1	
0.081112	0.016545	1

Residual Analysis

Expected Value: The following are normalized parameters with an expected value of 0.0. Values are in units of standard deviations from the expected value.		
Serial Correlation:	1.4678	indicates a systematic, non-random trend in the residuals
Skewness	-4.5827	indicates the likelihood of a few large negative residuals having an unduly large effect on the fit.
Kurtosis:	-1.8923	indicates the presence of a few large residuals of either sign
Weighting Factor:	0	
Heteroscedacticity:	-1.106	
Optimal Weighting Factor:	-1.106	

We see from the above output that we obtained a rather good fit of the curve to the data. In particular, the confidence limits of the parameters vary by around 1% at the most. Considering that the data set may be in error by as much as about 1.5%, these results are quite good. The Model Selection Criterion for this fit is greater than ten which also indicates that the curve fits the data quite well. We therefore conclude that we have obtained reasonably good values of the reaction rates K1, K2 and K3. The plot of the fitted curve and the data set is shown in Figure 15 below.

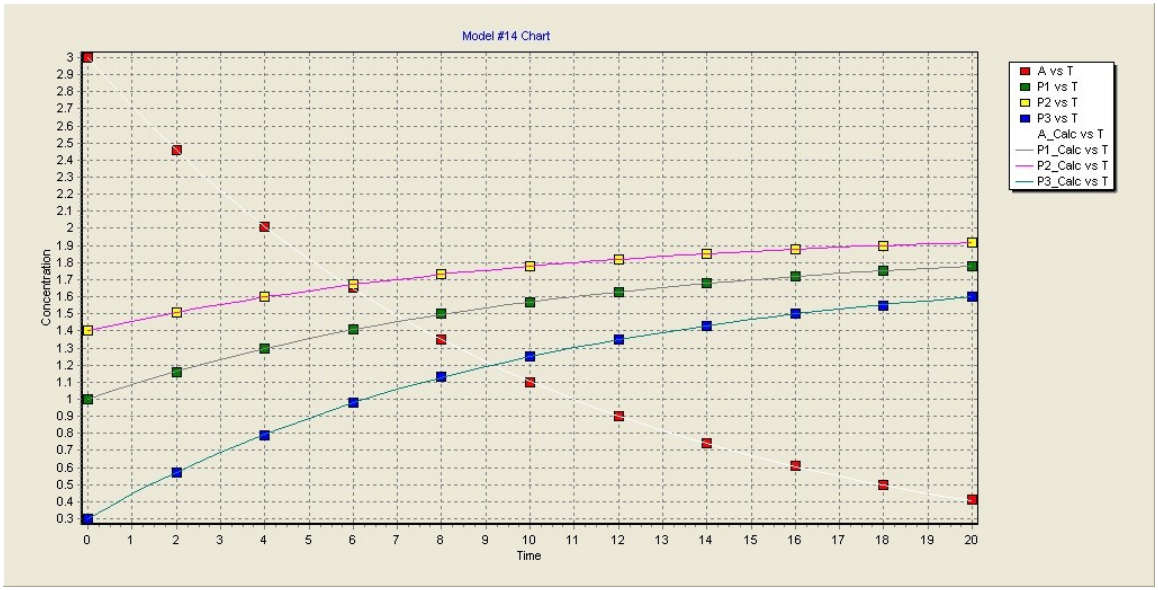


Figure 14.1 – Model #14 Parallel First-Order Irreversible Reactions